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Microstructure and properties of copper composite containing in situ NbC reinforcement: Effects of milling speed

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ABSTRACT

This paper presents a study on the effects of milling speed on the properties of in situ copper-based composite produced by mechanical alloying followed by cold pressing and sintering. A powdered mixture of copper, niobium and graphite with the composition of Cu–30%NbC was milled at various speeds (100, 200, 300 and 400 rpm). The NbC phase started to precipitate in the as-milled powder after 30 h milling at 400 rpm and the formation was completed after sintering at 950 °C. Enhancements of NbC phase formation with a reduction in Cu crystallite size were observed with the increase of milling speed. Density, hardness and electrical conductivity of the sintered composite were evaluated. An increase in milling speed resulted in an increase in sintered density and hardness but a reduction of electrical conductivity. The changes in the properties were correlated to the formation of NbC phase and refinement of copper and niobium carbide crystallite size since higher milling speed is associated with higher kinetic energy per hit.

1. Introduction

The excellent electrical and thermal conductivities of Cu coupled with superior hardness and a high melting point of niobium carbide phase provide good properties for an electrical conductor, spot welding electrodes, and contact materials. Metal matrix composite (MMC) with these properties has been widely produced by powder metallurgy (PM). The PM route involves mixing or blending the metal powder with ceramic powder, compacted into a desired shape and sintered under appropriate conditions. However, this conventional method led to high cost reinforcing phase preparation and poor interface bonding between reinforcement and metal matrix. Single stage processing using an in situ technique, which involves synthesizing the reinforcement phase in metal matrix by chemical reactions during MMC fabrication [1], can overcome such constraints. The in situ formation of reinforcement particles is able to enhance the mechanical properties of the copper matrix composite.

Mechanical alloying associated with powder metallurgy has been identified as a suitable method for producing in situ MMC. Mechanical alloying has the unique feature of producing MMC in nanostructure form by severe deformation of powder particles using high-energy milling force. The properties and structure of mechanically alloyed composite is highly dependent on the milling time, ball-to-powder weight ratio, milling media and milling speed [2]. As proposed by Abdellaoui and Gaffet [3,4], varying the collision velocity by varying the milling speed may influence the kinetic energy between powder and milling media in a planetary mill according to Eqs. (1) and (2):

$$||\overrightarrow{V_C}||^2 = (R\Omega)^2 + (r - r_b)^2\omega^2\left(1 + \frac{2\omega}{\Omega}\right) \quad (1)$$

$$E_k = \frac{1}{2}m\,||\overrightarrow{V_C}||^2 \quad (2)$$

where R is the distance between the disc center and the vial center, r is the vial radius, r_b is the ball radius, Ω is the disc rotation speed, ω is the vial rotation speed and m is the ball mass. Faster ball mill rotation transfers more impact energy to the powders during the collision event [5] and therefore influences the phase formation and properties of the composite, as noted by Rochman et al. [6], who concluded that properties and microstructures of as-milled Fe–Mn–C powder and hot pressed compact are correlated to milling speed. Low milling speed may lead to incomplete phase formation, so the desired properties of the powder cannot be achieved. For example, Ebrahami-Purikani and Kashani-Bozorg [7] reported that the intermetallic phase of Mg_2Ni was only detected after increasing milling speed up to 600 rpm.

However, high milling speed may increase the rate of contamination inside the vial. When the milling activity increases with high milling speed, temperature rises and at the same time excessive wear takes place on the milling media and the milling jar. To the authors' knowledge, there has been no report in the literature on

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the effect of milling speed on the NbC reinforcement formation and the properties of the in situ copper-based composite prepared by mechanical alloying. Therefore, the present study investigates the influence of different milling speeds on the formation of niobium carbide phase in a copper matrix when using the in situ fabrication method by mechanical alloying. The correlation between milling speed and the properties of the sintered composite is discussed.

2. Experimental procedure

Copper powder (99.7% pure, <63 μm), niobium powder (99.8% pure, <15 μm) and graphite powder (99.8% pure, <0.1 mm) were used as raw materials. A mixture of Cu–24.11 wt%Nb–3.11 wt%C, which corresponds to Cu–30%NbC, was milled together using a high-energy Fritsch Pulverisette P-5 planetary mill for 30 h. Four different milling speeds, i.e. 100, 200, 300 and 400 rpm, were set to investigate the influence of each milling speed on reinforcement phase formation and bulk properties of the resultant composite. A stainless steel milling ball with 20 mm diameter was used with a fixed 10:1 ball-to-powder weight ratio. After milling at each pre-set milling speed, the as-milled powder was investigated by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM).

For the powder consolidation process, the as-milled powder was compacted in a cylindrical stainless steel die at 300 MPa and sintered at 900 °C for an hour in a tube furnace under argon flow. XRD analysis and SEM observation were done to investigate the formation of NbC and the microstructure of the in situ composite. The crystallite size and internal strain of Cu and NbC phase in the as-milled and sintered composite were evaluated using the Williamson–Hall method as shown in the following equation [8]:

$$B_r \cos\theta = \frac{0.89\lambda}{D} + 2\eta\sin\theta \qquad (3)$$

where θ is the Bragg angle, D is the average crystallite size, B_r is the line broadening, λ is the X-ray wavelength and η is the internal strain. The lattice parameter of copper was calculated based on Cohen's method [8]. Vickers microhardness was used with a load of 500 g and 15 s dwell time to measure the hardness of the composite. Electrical conductivity was measured using a four-point probe technique while sintered density was measured using Archimedes' principle.

3. Results and discussion

3.1. Microstructure evolution

As shown in Fig. 1, XRD patterns of mechanically alloyed Cu–Nb–C powder at various milling speeds strongly displayed copper phase at diffraction angles of 43.3°, 50.4° and 74.1°. At 100 rpm milling speed, peaks for Cu, Nb and C phases are clearly observed, and their intensities decreased with increasing milling speed. The graphite peak starts to disappear when the milling speed is higher than 100 rpm. Intensity of Nb peaks is reduced and broadened and finally disappears after milling at 300 rpm, indicating that Nb is completely dissolved in the Cu matrix since only the copper phase remained after milling at 400 rpm, yet with a broadened peak. The disappearance of graphite and niobium phases is due to refinement and diffusion of both elements, leading to solid solution formation.

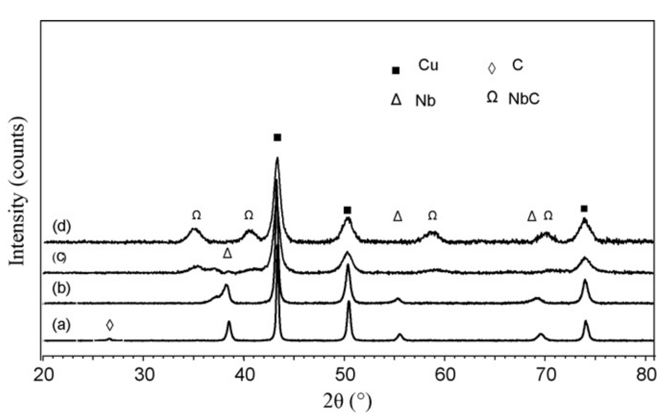

Fig. 1. XRD patterns of Cu–Nb–C powder as-milled with milling speeds of (a) 100, (b) 200, (c) 300 and (d) 400 rpm.

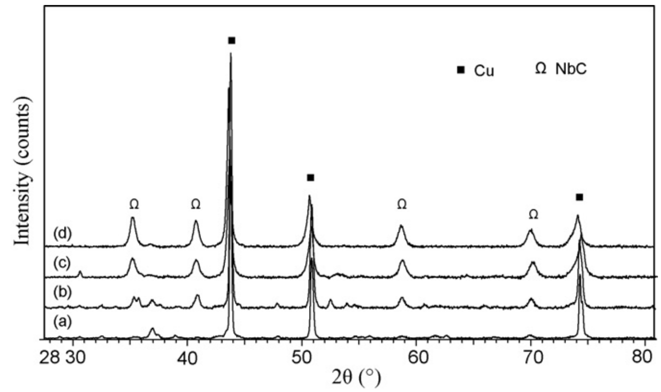

Fig. 2. XRD patterns of sintered Cu–Nb–C compact sintered at 900 °C with milling speeds of (a) 100, (b) 200, (c) 300 and (d) 400 rpm.

A similar observation has been reported by Marques et al. [9], who found that C is dissolved into the Cu lattice structure by forming a solid solution of Cu(C). Furthermore, Nb particles experience refinement since it is a brittle metal and easily fractured during milling unlike soft copper particles, which experience plastic deformation [10].

The XRD pattern shows that the NbC phase starts to form during mechanical alloying of Cu–Nb–C mixture at 300 rpm. The NbC peak becomes more intense and clearly defined after mechanical alloying at 400 rpm. This trend suggests that the NbC phase has been formed and its composition increases gradually with increasing milling speed. NbC did not form at a lower milling speed because the kinetic energy is insufficient for Nb to react with C to form NbC phase during ball-powder collision.

Fig. 2 shows XRD patterns of sintered Cu–Nb–C compact at different milling speeds. It was observed that Cu diffraction peaks broadened with increasing milling speed. NbC peaks were displayed after milling at 200 rpm and gradually increased with higher milling speed. This finding is in contrast to the case of as-milled powder, where the NbC phase was identified after milling at 300 rpm. This discrepancy may be attributed to the heat applied to the Cu–Nb–C during sintering that contributed to the formation of NbC. This result suggests that without applying heat, the internal energy of the particles obtained during mechanical alloying at 200 rpm is not enough to initiate the reaction to form NbC. Higher deformation of particles at a higher milling speed also facilitates the formation of NbC during sintering. Thus, a higher intensity of NbC peaks was observed for milling at 400 rpm.

Crystallite size and internal strain of Cu for the Cu–Nb–C mixture after milling and after sintering are shown in Fig. 3. Cu crystallite size for the as-milled powder decreased with increasing milling

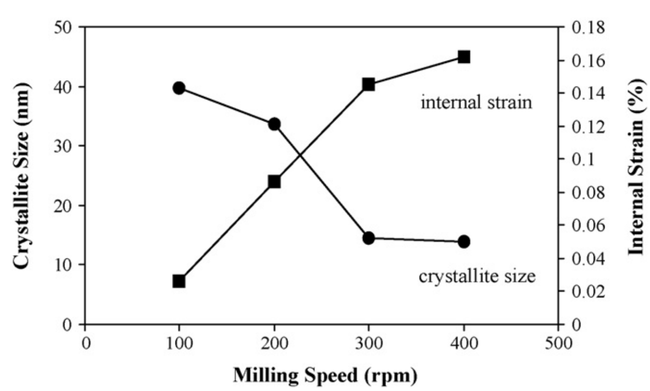

Fig. 3. Crystallite size and internal strain of Cu for as-milled Cu–Nb–C powder with different milling speeds.

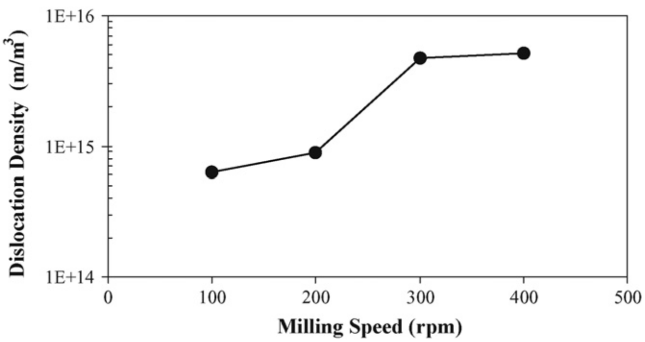

Fig. 4. Dislocation density of as-milled Cu–Nb–C powder at different milling speeds.

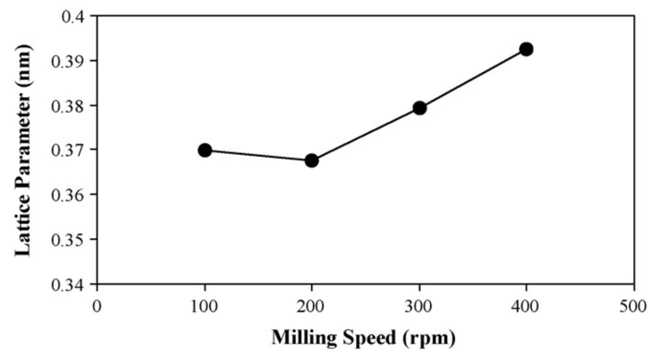

Fig. 5. Lattice parameter of Cu for Cu–Nb–C powder at different milling speeds.

speed. At 100 rpm, the mixture received the least effect from incoming impact energy. Boytsov et al. [11] have noted that increased milling speed or shock energy during mechanical alloying may cause a decrease in crystallite size of pure copper since the higher energy transferred to the powder with increased ball impact energy resulted in greater fracturing of the powder than that caused by cold welding at lower milling intensity. Another reason for the decreased crystallite size is the presence of extensive defects such as dislocation within a grain. According to Raghu et al. [12], if we assume that at least one dislocation occurs per crystallite, dislocation density is the inverse square of crystallite size:

$$N = (D)^{-2} \tag{4}$$

where N is the dislocation density and D is crystallite size. At a lower milling speed the dislocation density is low (Fig. 4), suggesting little deformation. After reaching a speed of 300 rpm, there is a slight increase in dislocation density. Aguilar et al. [13] explained that it

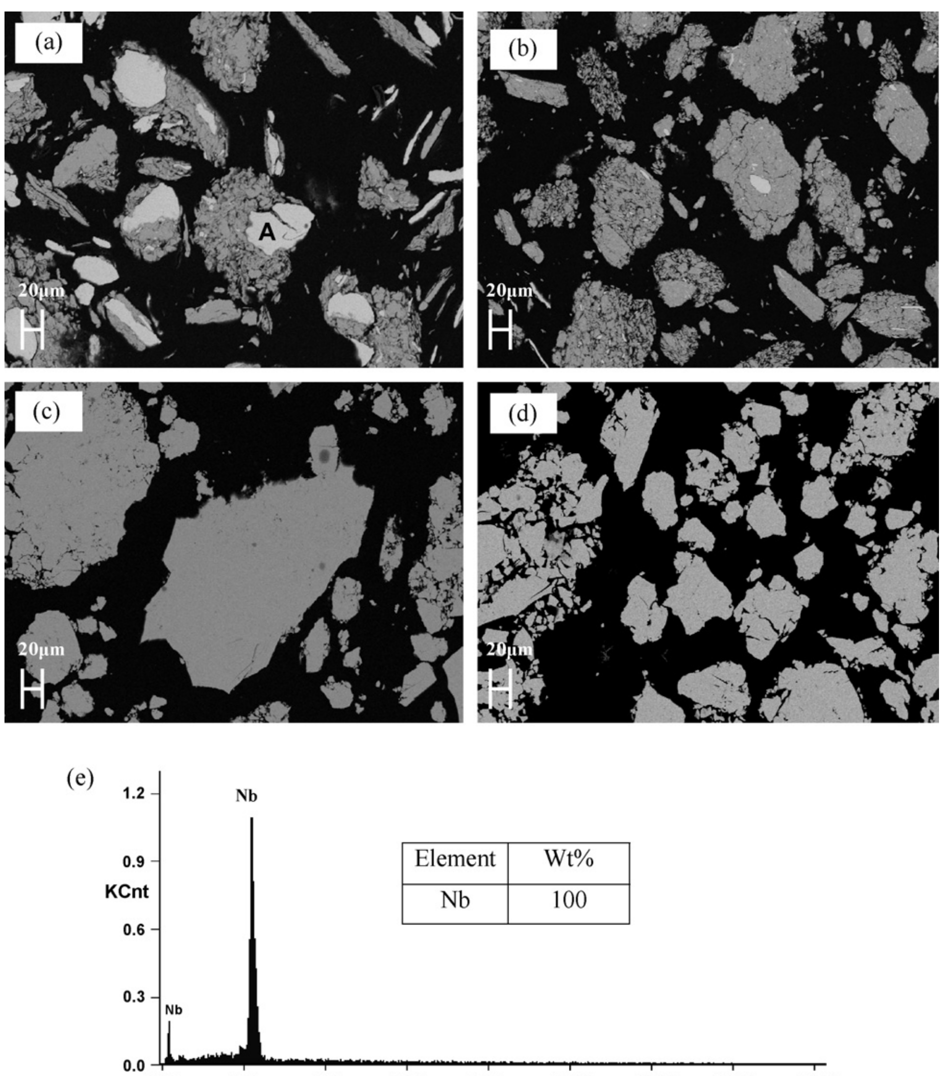

Fig. 6. SEM images of Cu–Nb–C powder at milling speeds of (a) 100, (b) 200, (c) 300 and (d) 400 rpm and (e) corresponding EDX spectra of area A.

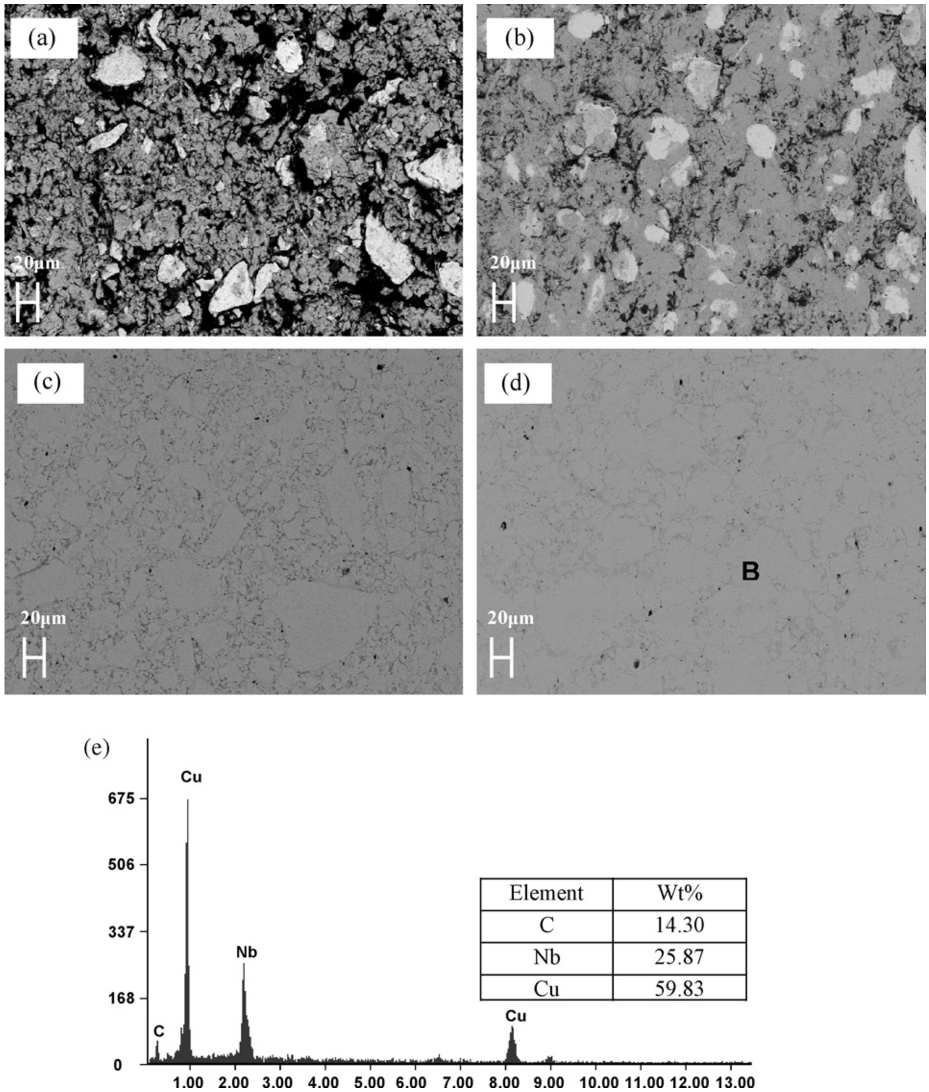

Fig. 7. SEM images of sintered compact Cu–Nb–C at milling speeds of (a) 100, (b) 200, (c) 300 and (d) 400 rpm and (e) corresponding EDX spectra of area B.

is difficult to generate dislocation with finer crystallite size. Hence, at 400 rpm not much dislocation is generated (Fig. 3).

Fig. 5 shows the dependence of the lattice parameter of Cu in the milled Cu–Nb–C powder as a function of milling speed. As would be expected, the dissolution of Nb with its larger atomic radius and of C into the copper matrix led to an increase in the copper lattice parameter [14]. Another possible reason for the dissolution of Nb and C in the copper matrix is that defects may have been introduced in the strained area [15] by the heavy impact energy of milling [5]. These defects would in turn facilitate the dissolution of Nb and C in copper.

Fig. 6 shows SEM images in backscattered mode of as-milled Cu–Nb–C powder with different milling speeds. When milling was performed at 100 and 200 rpm, obviously some of Nb particles were still not embedded in the Cu matrix as confirmed by EDX reflections at area A (the white area in Fig. 6), which showed the white area to be 100% Nb. At this stage, the fracture of Nb particles had not occurred, thus not all Nb had become embedded in the plastically deformed Cu matrix. This situation differs from Fig. 6(c) and (d) where the grey area becomes a dominant phase, indicating that the Nb is dissolved and a Cu solid solution is formed at higher milling speed.

Fig. 7 shows SEM images of sintered compact with EDX spectra spotted on the selected area of the composite. At milling speed of 100 and 200 rpm, the Nb phase could obviously be recognized as the white area, which indicated that Nb particles were not completely dissolved into the Cu matrix. At 200 rpm milling, however, Nb particles were surrounded by Cu and embedded in the matrix region (grey area) by fracturing and cold welding of particles. Higher ball-to-powder collision as a result of higher impact energy easily embedded the reinforcement into the matrix and Nb particles became more homogenously distributed, as illustrated by Fig. 7(c) and (d). This is indicated by EDX analysis of area B, which shows the composition of both the Cu matrix and the NbC reinforcement. The increased elimination of pores at 400 rpm compared to that at 300 rpm milling suggests that better densification of the in situ Cu–NbC composite was achieved by mechanical alloying of the Cu–Nb–C mixture at 400 rpm milling speed, coupled with appropriate compaction and sintering processes.

3.2. Density measurement

The average density values of green and sintered compacts of Cu–Nb–C are shown in Fig. 8. The green compact exhibits a lower density than that of the sintered pellets. This may be due to the presence of pores inside the composite body. The density of the green body is low because pores were not fully eliminated due to plastic deformation in the powder upon consolidation. During sintering,

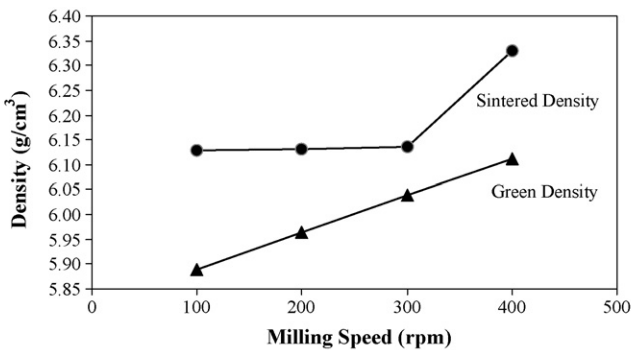

Fig. 8. Green density and sintered density of Cu–Nb–C compact at different milling speeds.

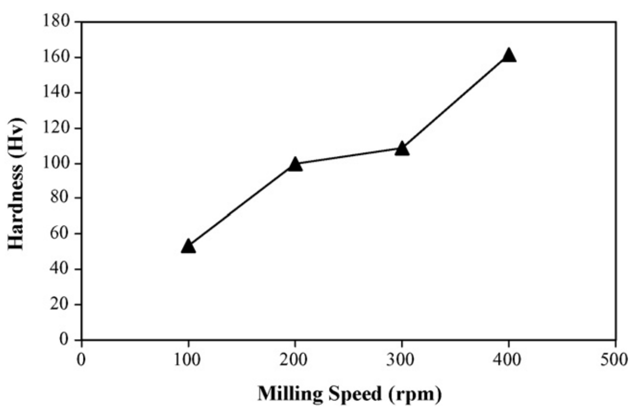

Fig. 9. Hardness properties of compact sintered Cu–Nb–C at different milling speeds.

atom diffusion occurred and reduced the presence of pores. Hence, higher density is attained by the sintered compact. This result can be explained by powder refinement of particles which was caused by higher kneading during mechanical alloying, lowering the distance between particles. As a result, densification during sintering was improved [16].

Based on Fig. 8, the density of the green compact tended to be linearly correlated with milling speed. However, sintered compact did not show a similar trend with regard to milling speed. The composite milled at 400 rpm speed yielded a much higher sintered density than did milling at other speeds. These results indicate that sintered density does not rely only on the green density but also on other factors such as powder size and residual Nb. As shown in Fig. 6, milling at 400 rpm produced the finest powder. Thus, this composite gave the highest sintered density because the intensity of the solid state densification depends on the mean size of the composite particles [17]. Besides, the residual Nb particles in the composite powder milled at 100 rpm and 200 rpm (Fig. 6(a) and (b)) also inhibited the sinterability of both composites by reducing the diffusion transport process during sintering.

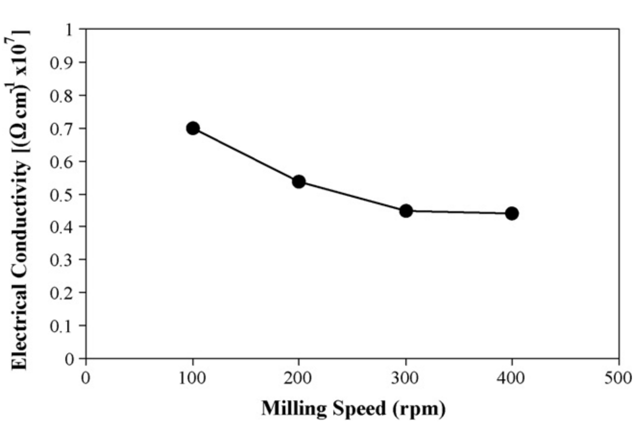

Fig. 10. Electrical conductivity of compact sintered Cu–Nb–C at different milling speeds.

3.3. *Hardness of sintered compact*

The increase in microhardness value of the composite is mainly attributed to the increase in the amount of NbC phase in the copper matrix, along with the increase in milling speed (Fig. 9). It is clear that the formation of hard NbC particles in the soft copper matrix increases the hardness of the Cu–NbC composite. According to Orowan's mechanism, the enhancement of hardness in a composite is attributed to the dispersion of NbC particulates in the copper matrix, which allows the particulates to become obstacles to the movement of dislocation [18]. High milling speed promotes the formation of finer NbC particles which are well distributed in the Cu matrix. Consequently, formation this finer NbC particles improved the hardening mechanism in the in situ composite.

3.4. *Electrical conductivity*

As illustrated in Fig. 10, the electrical conductivity showed a monotonous decrease corresponding to the increase of milling speed. Cu crystallite size is one of the causes influencing the electrical conductivity of the Cu–NbC composite. Finer crystallite size is obtained at higher milling speed as the mixture has higher kinetic energy, leading to the higher incidence of various crystal defects like dislocation and Cu grain boundaries. Restriction on the movements of electrons at these defects lowers the electrical conductivity of this composite. Another possible reason for a decrease in electrical conductivity is related to the refinement of NbC formation at higher milling speed in Cu matrix because finer NbC particles disturb the electron flows by acting as electron scattering centers.

4. Conclusion

The XRD diffraction pattern showed that the NbC phase in the as-milled powder was formed during milling at 300 rpm and its intensity increased with higher milling speed. Sintering at 900 °C of the Cu–Nb–C compact enhanced the NbC peaks in XRD patterns. Composite prepared at higher milling speed showed higher green density and sintered density due to refinement of mixture particle size. Microhardness correlated to the refinement of the powder that had been attained at higher milling speed. The composite milled at 400 rpm milling speed gave the best properties in density and hardness. The electrical conductivity of the composite decreased with increased milling speed due to the refinement of particles and the strain hardening which are associated with mechanical alloying.

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